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BIRTH, DEATH AND TRANSFIGURATION: THE SYNTHESIS OF
PRECERAMIC POLYMERS, THEIR PYROLYSIS AND THEIR CONVERSION
TO CERAMICS

by

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→ Inorganic and organometallic polymers are those macromolecular systems in which the polymer backbone contains elements other than the carbon, oxygen and nitrogen usually found in organic polymers.¹ To take as an example silicon-containing polymers, in the silicones the polymer backbone is composed of the Si-O repeat unit; in polysilazanes, of the Si-N unit; in polysilmethylenes, of the Si-C unit. In the polysilanes there are only silicon atoms in the polymer backbone. When one considers that many of the other metalloids and metals among the elements in the Periodic Table have been or, in principle, can be incorporated into polymeric systems, then it is clear that the field of inorganic and organometallic polymers is a very large one indeed. Inorganic and organometallic polymers have been of interest to chemists for a long time. It was the commercial development of the silicones in the 1940's that gave this field of research its modern impetus.² Once it was appreciated how useful these versatile organosilicon polymers could be, with a long list of applications that is still growing today, chemists became interested in the possibility of developing other organometallic (and also inorganic) polymers, ones that might complement or even surpass the



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silicones as far as useful applications were concerned. Research on inorganic and organometallic polymers became very active in the 1950's and 1960's. Work in this area became an international effort, prompted by the need for new materials that would meet the exacting demands of the jet age that had effectively commenced around the end of World War II. Even greater demands, in terms of materials that would still be useful under extreme conditions, came with the dawning of the space age on October 4, 1957 with the launching of Sputnik I.

We do not mean to give the impression that inorganic and organometallic polymers were unknown before the 1940's. Indeed, polymers of the type $(R_2SiO)_n$ had been prepared by Kipping and his students during the period 1910-1935, but their potential importance in terms of useful applications was not recognized. Kipping was able to work in this area without competitors, although there was interest on the part of other research groups in the monomeric compounds of silicon. Some organometallic polymers went unrecognized as such for a long time: it must be remembered that macromolecular chemistry is a relatively new field. Thus the dialkyltin oxides were first prepared in 1854, but their polymeric nature was not recognized until nearly one hundred years later.³ The research on inorganic and organometallic polymers carried out in the 1950's and 1960's covered a broad range: other organosilicon polymers such as the polysilazanes; polymetalloxanes; various boron-containing polymers including those derived from the very stable carboranes; polyphosphazenes; coordination polymers; metal-containing polyesters, polyamides and vinyl polymers. In all of these investigations it was the polymer per se that was of interest. The objective in most cases was a polymeric material whose properties at extremes

of temperature would surpass those of the conventional organic polymers. Most of all, high thermal stability was the goal that all strove to achieve. Other properties, of course, were of interest: elasticity at low temperature, adhesion, flexibility, lubricity, resistance to aviation fuels, resistance to oxidation and other forms of chemical attack, and others. Although a few potentially useful materials were developed in these years, for instance, the new generation of polyphosphazenes⁴ and the poly(carboranylenesiloxanes)⁵, for the most part the yield of all this research in terms of useful inorganic or organometallic polymer systems was negligible, and eventually research support in this area effectively "dried up."

The picture changed again in the 1980's when ceramics as potential replacement materials for metals and metallic alloys in many applications and also as "high technology" materials with completely new applications began to attract worldwide attention.⁶ While much effort was and still is devoted to improving the reliability of ceramic components made from oxide and non-oxide ceramics by innovations in ceramics processing, it was the development of composites that has driven ceramics technology to new levels.⁷ Composites are combinations of materials that consist of one or more reinforcing materials (glass fibers, carbon fibers, etc) in a matrix (polymer, metal, glass, ceramic, etc.) that binds the reinforcement materials together. Composite materials have greater strength and toughness than the matrix material alone and have found wide applications in the aerospace industry. In fact, composite materials can be fabricated that are lighter in weight and have higher strengths than many metals. Since ceramics have high thermal stability but are inherently brittle materials, it was the anticipated benefits of fabricating components from ceramic-ceramic composites that has been the

driving force behind the recent interest in ceramics as structural materials for use in harsh environments. However, prior to 1980 there were few reinforcing materials commercially available for fabricating ceramic-ceramic composites, and those that were available did not meet the high-temperature requirements for some desired applications. It is in the area of composites that inorganic and organometallic polymers find many new and important applications. But these applications are not ones involving the polymers themselves, but rather, in the end, of their pyrolysis products, ceramic materials. Hence after synthesis (birth) come pyrolytic decomposition (death) and conversion to a ceramic (transfiguration). This leads to the name "preceramic polymer".⁸

To understand the importance of composites in the context of modern materials science, consider the stress/strain behavior of a monolithic ceramic body as obtained by conventional ceramics processing (Fig. 1, curve 1), of a particulate or short fiber ceramic matrix composite (curve 2) and of a continuous fiber ceramic matrix composite (curve 3).⁹ The "conventional" ceramic shows catastrophic failure. The situation is greatly improved in the case of the particulate or short fiber composite. This material is tougher, but it still shows catastrophic failure. In marked contrast, the continuous fiber composite has the great advantage of not undergoing catastrophic failure. It shows substantial retention of strength past the point of initial matrix failure, with slow, rather than abrupt, degradation of strength as a result of the energy dissipation processes during crack advance provided by the presence of the strong, high modulus (stiff) ceramic fibers.

Complex ceramics processing issues must be addressed in the manufacture of strong continuous fiber ceramic matrix composites. It is

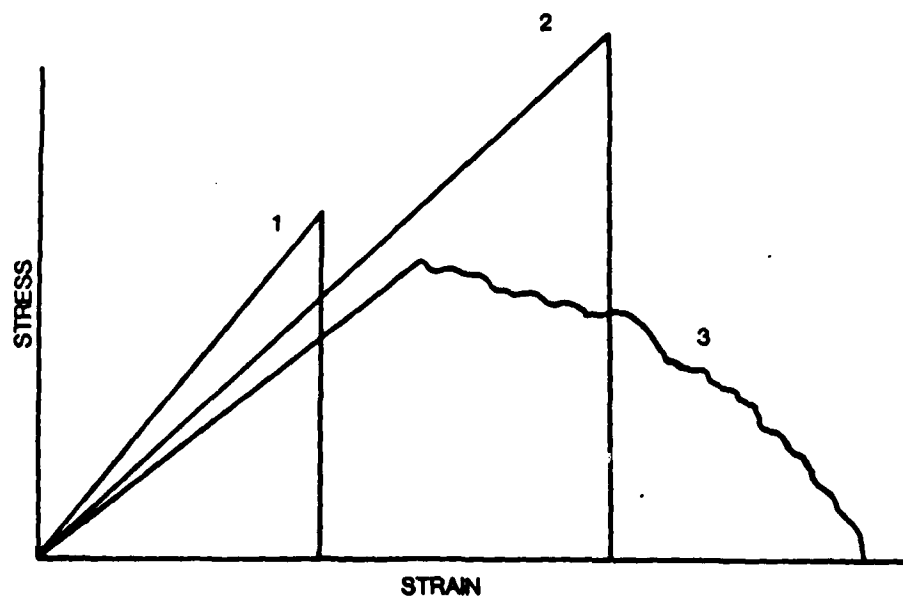


Fig. 1 Comparison of stress/strain curves for various ceramic bodies.

beyond the scope of this brief article to discuss these; our focus is on the inorganic and organometallic preceramic polymers. In continuous fiber composites the ceramic fibers may be present in the form of filaments that usually are positioned unidirectionally, bidirectionally or multidirectionally in a ceramic matrix. Among the fabrication techniques that may be used for such ceramic matrix composites are hot pressing, chemical vapor infiltration, reaction bonding and polymer infiltration/pyrolysis. Thus the inorganic or organometallic polymer can play a role as the precursor for both the fiber and the matrix. Such polymers can, in principle, find another important use in the fabrication of continuous fiber ceramic matrix composites. To achieve optimum strength and toughness, there must be only weak, controlled chemical interaction between the fibers and the matrix material. To prevent strong fiber-matrix bonding, the fibers may have to be coated with a material that does not interact chemically with the matrix. Such coatings can be applied on the fibers by chemical vapor deposition, but they also can be formed by pyrolysis of a polymer coating on the fiber.

Finally, there is the problem of carbon/carbon composites, whose superior strength and thermal stability make them prime candidates for many "high tech" structural applications, but whose high temperature applications are compromised in the atmosphere by their ready oxidation. Here also, inorganic and organometallic preceramic polymers can find an important application. If pyrolysis of the polymer leads to a refractory and chemically inert ceramic, especially one that is stable to oxidation at high temperatures, then infiltration of the pores of the carbon/carbon composite and coating of its surface with this polymer, followed by pyrolysis, should give a protective coating that will allow use of the carbon/carbon composite with full benefit of

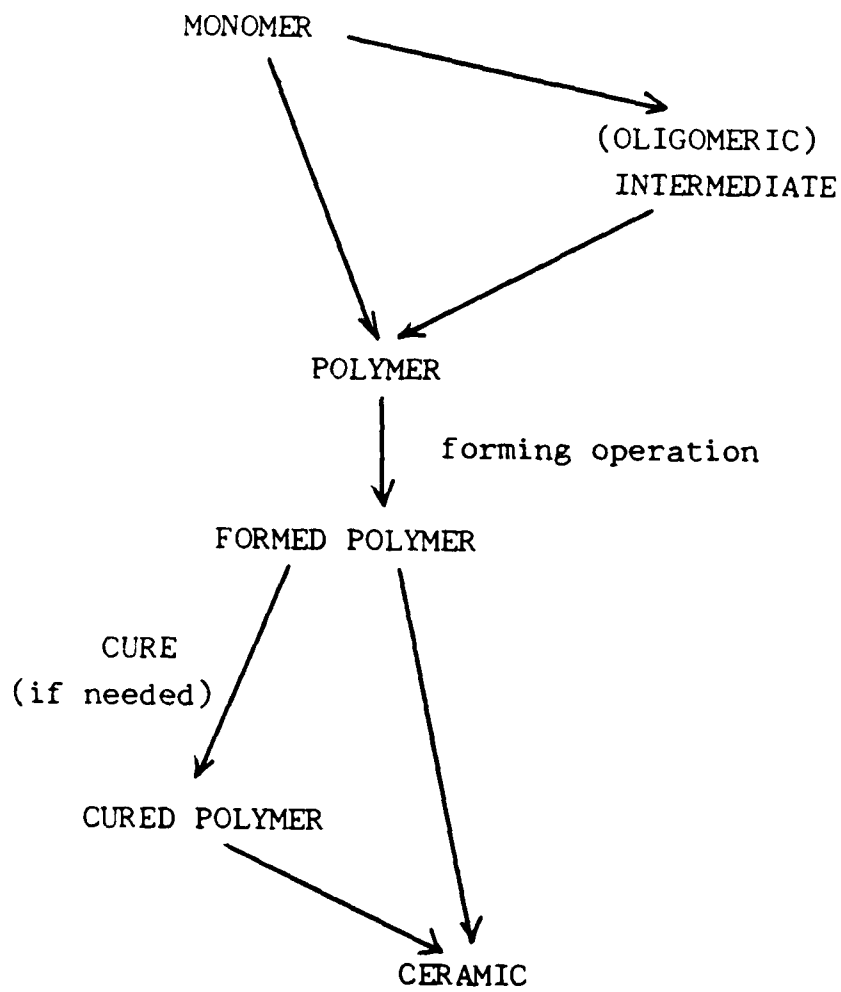
its inherently high strength and thermal stability under otherwise hostile conditions. The use of polymer-derived ceramics to protect other surfaces such as those of reactive metals against chemical corrosion or oxidation at high temperatures also is a possibility. Such ceramic coatings, as formed by polymer pyrolysis, also can serve to strengthen the material they are coating. Thus, it was reported recently by workers at SRI that a polysilazane-derived coating on glass rods made them about 3.5 times stronger.¹⁰

A further application of inorganic and organometallic preceramic polymers of potential commercial importance is found in the area of conventional ceramic processing: in their use as binders in ceramic powder processing. Binders are used primarily to help ceramic powder particles adhere to one another. Both the green strength of a ceramic body and its green density are affected by the binder used. Although many types of materials have been employed as binders in ceramic powder processing, organic polymers, such as, for instance, polyvinyl alcohol, polyvinyl butyral, polyethylene and poly(methyl methacrylate), have traditionally played an important role in binder formulations.¹¹ While the use of such materials as binders often results in achievement of high green body strength and/or high green body density, there also can be some drawbacks associated with their use. Major problems can be encountered upon firing of the ceramic body due to binder burnout. Cracking of the part can result when the temperature range of the binder decomposition is narrow, so that most of the volatiles produced in its pyrolysis are released practically simultaneously. Furthermore, binder burnout can contribute to formation of voids in the microstructure of the final ceramic body. Such voids, which also can result from poor packing of the ceramic powder particles, can act as stress concentrators, and thus facilitate

the catastrophic failure shown in Figure 1. Usually, but not necessarily always, a drawback is that during the non-oxidative firing of the ceramic body there can be substantial retention of carbon, either due to incomplete polymer binder pyrolysis (giving nonvolatile carbonaceous residues) or due to polymer-ceramic surface bond formation which prevents degradative volatilization of the binder. In order to avoid these problems, ceramists more recently have become interested in "low loss" inorganic or organometallic polymeric binders. The polymers of choice are those whose pyrolysis gives a high yield of ceramic residue with release of a minimum quantity of potentially destructive volatiles. Preferably, this ceramic residue also will be the same material of which the powder is composed, but this is not an essential requirement. It can be a different material but still a useful one: to control sintering or grain boundary chemistry. By use of such "low loss" binders one may hope to achieve not only the desired high green body strength and density that use of organic binders brings, but also one may hope to obtain ceramic parts of high strength and density. To date, most "low loss" organometallic binders that have been investigated have been organosilicon polymers. These are used as binders for silicon carbide and silicon nitride powders.

These then are the major applications of inorganic and organometallic preceramic polymers: as precursors for ceramic fibers, coatings and matrices and as binders for ceramic powders. Let us now consider the preparation of preceramic polymers and the requirements in terms of their chemical and physical properties that must be met. Scheme 1 brings a simple flow-diagram of the processes involved in the preparation and utilization of a preceramic polymer. Chemistry, it may be noted, plays an important role in all steps.

SCHEME 1



First and foremost, the preceramic polymer must be processable. All of the applications discussed above require a polymer that is soluble in an organic solvent and/or meltable, so that it can be spun into fibers, formed into a coating by various means, infiltrated into a fiber preform or coated onto ceramic powder particles. Many known inorganic and organometallic polymers are immediately eliminated from consideration because they are intractable: neither soluble nor meltable. This does not mean that an intractable polymer is useless; it means only that it cannot be used for any of the special applications mentioned above. In fact, several commercial processes for the preparation of very pure silicon nitride powder involve the synthesis and subsequent pyrolysis of an intractable polymer. In these processes the reaction of silicon tetrachloride with ammonia, carried out in an organic solvent or by using the reactants in liquid or gaseous form, produces "silicon diimide", $[\text{Si}(\text{NH})_2]_x$, as an insoluble and infusible white polymeric solid. When pyrolyzed, this material loses ammonia to give first amorphous silicon nitride and then, at higher temperatures, crystalline $\alpha\text{-Si}_3\text{N}_4$.¹²

Another important requirement is that pyrolysis of the inorganic or organometallic preceramic polymer give as large a yield of ceramic residue as possible. Ceramic yields ($= \text{weight of ceramic residue} \times 100 / \text{weight of pyrolysis charge}$) of 60-75% are acceptable, but higher ceramic yields of 80% or greater are desirable. Most polymers that have an inorganic backbone contain substituents on some or all of the backbone atoms. These often are hydrogen atoms or organic groups, but they can be of other types. During the pyrolysis of the polymer these substituents may become incorporated into the ceramic residue or they may be eliminated in the form of volatile, low molecular weight compounds that escape as gaseous products at the high pyrolysis

temperatures. Thus H and CH₃ are preferred substituents since their loss will leave a high ceramic residue (if the backbone atoms are retained). The pyrolysis of a polymer may give the theoretical yield of a ceramic as represented by the backbone atoms, but if the ceramic yield is low because of the large contributing weight to the pyrolysis charge of rather heavy substituents that will end up as volatiles, then useful applications of the polymer may be questionable. The high ceramic residue yield is of importance not from economic considerations. Rather, a high ceramic yield means that the quantity of gases evolved during pyrolysis will be small. These gases can be very destructive, especially if they are released over a narrow temperature range, causing cracking or even rupture of the ceramic part. So the fewer evolved gases, the better from the point of view of "good" ceramics. Also, the greater the weight loss of a preceramic polymer on pyrolysis, the greater will be the shrinkage of the residual body. However, shrinkage is unavoidable when a polymer is pyrolyzed to a ceramic since one is starting out with a material of low (1 g/cc or less) density and is forming a material of greater (2-3 g/cc) density.

The requirement of high ceramic yield on pyrolysis limits the types of polymers that will be useful precursors for ceramics. In general, linear, uncross-linked polymers are not suitable since their pyrolysis leaves little if any solid residue. When pyrolytic scission of a bond in the backbone of a linear polymer occurs, small molecules usually are formed in subsequent steps. These, being volatile, are swept out from the hot zone by the carrier gas. Such small molecule formation can occur by way of elimination of small unsaturated and unstable species such as R₂Si in the case of polysilanes and R₂Si=O in the case of silicones. Such intermediates then oligomerize, giving

mostly volatile, low molecular weight cyclic molecules that escape the hot zone. Alternatively, volatile products can be formed by "back-biting" of a chain end radical in an S_H2 process at an atom further down the backbone, a process that can form volatile cyclics. In any case, what is needed is a cross-linked system, optimally a network polymer, so that if one bond breaks on heating, many bonds remain to hold the system together in the hot zone. One might compare a "good" preceramic polymer to a tennis net: if a few strings of the net are cut, a useful structure still remains. On the other hand, the linear polymer is like a clothesline: if that is cut, the useful "structure" is lost. While a substantial amount of cross-linking is desirable, it should not be so extensive as to cause gelation of the polymer. As noted above, a soluble system is required for the initial processing. The ideal preceramic polymer is one that is cross-linked but still soluble and that still contains reactive functionality ("latent reactivity", in the words of Wynne and Rice^{8a}) that on heating will react to cause still further cross-linking to give the desired high ceramic yield. The design of a useful preceramic polymer thus requires the introduction of reactive functional groups at the monomer and/or polymer stage so that the initial stage of the pyrolysis results in formation of a highly cross-linked, nonvolatile, probably insoluble network, hence in retention of the elements of interest in the hot zone.

There are other requirements that must be met in order to have a useful preceramic polymer. There is the problem of elemental composition. At this point in the development of the chemistry of preceramic polymers, the preparation of very pure ceramics by polymer pyrolysis is not straightforward. It is not certain, in fact, what degree of purity is required for the applications enumerated above. In some cases, grossly impure systems will be

unsatisfactory. For instance, in the case of the preparation of silicon carbide, SiC, by polymer pyrolysis, one would like to achieve a 1:1 ratio of Si to C in the ceramic product. Depending on the precursor used, one might obtain on pyrolysis SiC plus a substantial amount of free carbon or SiC plus a substantial amount of free silicon (we have encountered both in our research). Neither alternative is acceptable. At the least, a large amount of free carbon in the ceramic product will bring problems of high temperature oxidation, but the free carbon could cause other, less obvious problems as well. On the other hand, a large amount of free silicon (mp 1414°C) would compromise the high temperature applications of the ceramic part. Effective control of the elemental composition of the final ceramic product can be achieved by manipulating the chemistry at the synthesis or even at the pyrolysis stage. In the synthesis of the preceramic polymer one can use appropriate mixtures of monomers so that pyrolysis gives a ceramic whose elemental composition is close to that desired. Alternatively, one can use a mixture of two polymers, in chemical or physical combination, so that pyrolysis gives the desired elemental composition. At this point, we cannot predict what elemental composition of the derived ceramic will be obtained on pyrolysis of an inorganic or organometallic polymer, so it is for the most part a matter of doing experiments until pyrolysis trends are recognized. This empirical approach does work and in our own organosilicon chemistry we have been able to prepare preceramic polymers whose pyrolysis gives ~99% SiC, ~99.5% Si₃N₄, or any mixture of the two by appropriate manipulation of the chemistry.

The preparation of essentially pure silicon nitride by polymer pyrolysis represents a special case that illustrates another important chemical

consideration: the choice of gas stream in the pyrolysis. Polymer pyrolysis usually is carried out in an appropriate furnace through which a gas is flowing. The gas stream serves two purposes: to protect the system from the atmosphere and to sweep away the volatiles produced in the pyrolysis. The gas used may be either an "inert" gas or a "reactive" gas. The pyrolysis of our polysilazane of composition $[(CH_3SiH_2NH)_a(CH_3SiN)_b]_x$ serves to illustrate the use of both types of pyrolysis gas stream.¹³ Pyrolysis of this polysilazane in a stream of argon (an inert gas) to 1000°C gives a black ceramic residue in 80-85% yield. This material is amorphous, so composition in terms of pure species such as SiC and Si₃N₄ is meaningless. However, the analytical results (%C, N, Si) can be used to calculate a hypothetical composition in terms of SiC, Si₃N₄ and free C. The results of such a calculation in one case were: 67% by weight of Si₃N₄, 28% SiC and 5% C. This may be close to the actual composition of this material when it becomes crystalline above 1450°C. In marked contrast, when this polysilazane is pyrolyzed to 1000°C in a stream of ammonia, a white solid residue is obtained. This usually contains less than 0.5% by weight of carbon and is almost pure silicon nitride. The chemistry that takes place at temperatures of 400-600°C to remove the carbon must be complex and is as yet not understood. Reactions at these temperatures of the decomposing polysilazane with ammonia or its decomposition products very likely are involved, but this question requires further study. We have used ammonia as the "reactive" gas to good advantage in the preparation of nitrides of other elements. For instance, polymers of the type $[B_{10}H_{12}\text{-diamine}]_x$, where "diamine" may be ethylenediamine or its various N-methyl derivatives, piperazine, triethylenediamine or propylenediamine, when pyrolyzed in a stream of argon to 1000°C, give a black solid residue whose "composition" can

be calculated from the elemental analysis as $1 \text{ B}_4\text{C} + 1 \text{ BN} +$ a minor amount of carbon. Pyrolysis in a stream of ammonia, on the other hand, results in formation of a white residue, essentially pure boron nitride, BN.¹⁴ Similarly, pyrolysis of $(\text{CH}_3)_2\text{N}$ -terminated $[\text{Ti}(\text{NR})_2]_x$ -type polymers in a stream of ammonia gives golden-yellow titanium nitride.¹⁵

It should be stressed that when we say "elemental composition" we mean just that: the results of an elemental analysis. At the usual final pyrolysis temperatures of 1000-1200°C the solid residue is amorphous according to powder X-ray diffraction. Thus the elemental composition has no meaning in terms of species present in the solid phase. Little is known about the amorphous solids produced in the pyrolysis of inorganic and organometallic polymers. ^{29}Si solid state nuclear magnetic resonance studies of the pyrolysis product of a polysilazane that contains silicon, carbon and nitrogen, as reported by workers from the Dow Corning Corporation laboratories, suggested that in these materials the silicon atoms are randomly bonded to carbon and nitrogen atoms, rather than being in "islands" of SiC and Si_3N_4 .¹⁶ Most of these amorphous ceramics crystallize when heated to 1400-1500°C and then, in the case of our polysilazane-derived amorphous silicon "carbonitride", X-ray diffraction lines due to $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-SiC}$ are observed. The amorphous, very porous, low density solids obtained in the pyrolysis of inorganic and organometallic polymers require further detailed study since in many applications it is these amorphous materials, not the crystalline materials that can be obtained from them, that are present.

As noted earlier, an important application of preceramic polymers is their use in the preparation of ceramic fibers. Most often, polymer fibers are spun from a melt of the the polymer (melt spinning). Alternatively, polymer

fibers can be spun from a solution of the polymer into a hot chamber in which the solvent is flashed off, leaving the fiber (dry spinning) or into a nonsolvent in which the fiber coagulates (wet spinning). Of these, melt spinning is preferred: it gives the strongest green fibers and it avoids the use of large volumes of solvent that must be recycled. Preceramic polymers intended for melt spinning require a compromise. If the thermal cross-linking process is too effective at relatively low temperatures (100-200°C), then melt spinning will not be possible since heating will induce cross-linking and will produce an infusible material in the heated polymer reservoir of the spinning apparatus prior to spinning. A less effective cross-linking process is needed so that the polymer forms a stable melt that can be extruded through the holes of the spinneret. The resulting polymer fibers, however, must then be "cured", i.e., rendered infusible, wholly or in part, so that the fiber form is retained on pyrolysis. Such cures may be effected chemically, most often by air oxidation or hydrolysis with moist air, but more complex chemistry can be applied. For instance, the polymer can be so designed that there will be residual Si-H and Si-CH=CH₂ groups that can be made to undergo reaction to give sufficient cross-linking to make the fiber infusible. The cure chemistry must be developed with care since it is important that the ceramic fibers be solid all the way through. Such cures may also be effected by radiation, and ultraviolet, electron beam and gamma irradiation have been used. The radiation cures have the advantage that they do not introduce oxygen as do the oxidative and hydrolytic cures.

Now that the main requirements for a useful preceramic polymer have been outlined, it will be of interest to consider the various inorganic and organometallic polymer systems that have been commercialized or whose

commercialization is in the development stage. Although the possibility of preparing ceramics by polymer pyrolysis was first discussed by Chantrell and Popper in 1964¹⁷, it was not until the mid-70's that the preparation of preceramic polymer fibers was reported. Verbeek of Bayer AG developed a precursor for $\text{Si}_3\text{N}_4/\text{SiC}$ based on the reaction product of methyltrichlorosilane and methylamine, $\text{CH}_3\text{Si}(\text{NHCH}_3)_3$.¹⁸ Thermolysis of this compound at 520°C resulted in formation of methylamine and other volatile products and left a brittle, transparent, yellow-brown "carbosilazane resin" that was soluble in organic solvents. This polymer could be melt-spun at 220°C to give fibers, which after a moist air cure step, could be pyrolyzed at 1200°C to give glistening, black ceramic fibers in 55% ceramic yield. When they were heated to 1800°C , crystallization to $\beta\text{-SiC}$ and $\alpha\text{-}$ and $\beta\text{-Si}_3\text{N}_4$ occurred. This process went to the pilot plant stage but apparently was not commercialized.¹⁹ It was the subject of further detailed studies by workers at NASA.²⁰ It is still of interest today and, in fact, other companies have obtained licenses to this technology. The structure of the "carbosilazane resin" is not known. One guess¹⁹, based on known silazane chemistry, especially the great tendency of silazane systems to form cyclic structures, is shown in Figure 2. Another polymeric precursor for $\text{Si}_3\text{N}_4/\text{SiC}$ ceramics, developed at about the same time by Winter, Verbeek and Mansmann at Bayer AG²¹, was based on the reaction of RSiCl_3 compounds or of mixtures of R_2SiCl_2 and RSiCl_3 compounds with ammonia. The resulting polysilazane (usually with $\text{R} = \text{CH}_3$) could be used as a binder for SiC powder, or to form, after pyrolysis, ceramic films, and, with the help of an organic polymer as a spinning aid, ceramic fibers. This process was not commercialized, but it has provided the basis for much derivative work in other laboratories around the world.

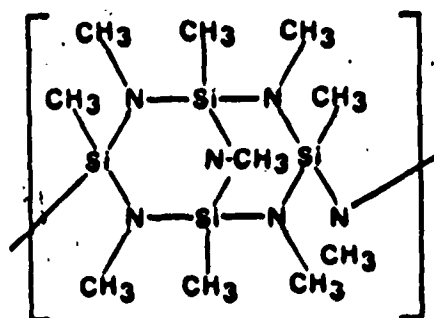


Fig. 2. METHYL-N-METHYLSILAZANE RESIN

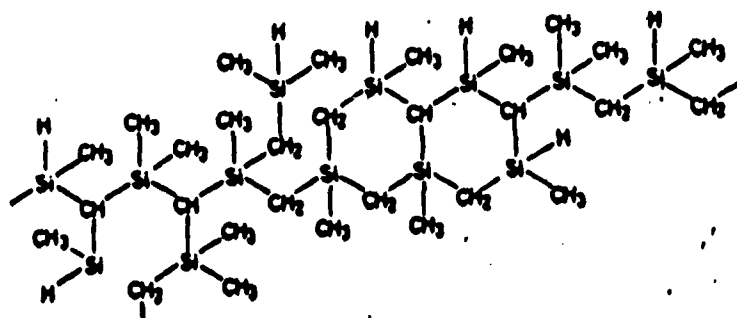


Fig. 3. Constitutional chemical formula of polycarbosilane.

An important early contribution to the area of preceramic polymers for silicon-containing ceramics was made by Yajima and his coworkers at Tohoku University in Japan, who developed a process that results in the formation of ceramic fibers of high SiC content.²² It is of interest to consider the novel chemistry that is the basis of this process. The initial step is the sodium condensation of dimethyldichlorosilane, $(\text{CH}_3)_2\text{SiCl}_2$, in xylene solution to give an insoluble poly(dimethylsilylene), $[(\text{CH}_3)_2\text{Si}]_x$. This polymer is not a useful preceramic material: its pyrolysis gives a very low ceramic yield. However, when this polymer is heated in an autoclave at 450-470°C, complex chemistry takes place and a useful polymer that may be melt-spun is obtained. This material no longer contains an all-silicon backbone; the thermal treatment has caused extensive structural changes. Nuclear magnetic resonance spectroscopic studies established that it has a complex structure, with one of the major components being the $\text{CH}_3(\text{H})\text{SiCH}_2$ unit. The presence of the $(\text{CH}_3)_2\text{SiCH}_2$ unit was also established, but the fact that pyrolysis of this polycarbosilane gives a 55-60% ceramic yield suggests that a cross-linked structure is present. We note that pyrolysis of a linear $[(\text{CH}_3)\text{HSiCH}_2]_x$ polycarbosilane gives a ceramic yield of only 5%.²³ The representative part-structure shown in Figure 3 was suggested by Yajima for his polycarbosilane. After this polycarbosilane resin had been melt-spun at around 350°C, the polymer fibers required a cure step before they could be pyrolyzed to ceramic fibers. This was effected by heating them in air at 190°C (but γ -irradiation also has been used to cure these fibers²⁴). When the cured fibers were heated to 1200-1300°C in an inert atmosphere, "SiC" fibers were obtained. These were shown by analysis to contain an excess of carbon (over "SiC") and some oxygen. The analytical results could be translated into a "composition" of

1 SiC, 0.78 C, 0.22 SiO₂. The silica is derived from the air cure. Crystallization of the amorphous ceramic occurred above 1200°C. Above 1300°C gaseous CO was evolved and the strength of the ceramic fiber was lost. A variation of this basic procedure in which the thermal treatment of the initial polysilane was carried out at atmospheric pressure in the presence of a borosiloxane was developed as well. In another variation, the Yajima polycarbosilane was heated with a titanium alkoxide, Ti(OR)₄, to give a more highly cross-linked titanium-containing polymer. Pyrolysis of this product resulted in formation of a ceramic material that contained titanium carbide as well as silicon carbide.

The ceramic fibers obtained by the Yajima procedure are produced (trade name, Nicalon) by the Nippon Carbon Company, the titanium carbide-containing fibers (trade name, Tyranno) by Ube Industries. Many studies of the Nicalon fibers have been published and their use in the fabrication of ceramic, glass and metal matrix composites is well documented. There are various problems associated with the use of the Nicalon fibers at high temperatures and the search continues for ceramic fibers with better high temperature properties.

Polymeric silicon carbide precursors, both polysilanes, have been developed by other companies. Schilling of the Union Carbide Laboratories in Tarrytown, NY has found the mixed monomer approach useful.²⁵ In his procedure a polysilane is prepared by the sodium condensation of 0.85 molar equivalents of trimethylchlorosilane, (CH₃)₃SiCl, 0.3 of methyldichlorosilane, CH₃SiHCl₂, and 1.0 of methylvinylchlorosilane, CH₃(CH₂=CH)SiCl₂ in a mixed hydrocarbon/ether solvent. The product polysilane, of composition (CH₃)₃Si[(CH₃)(H)Si]_x[(CH₃)(CH₂=CH)Si]_ySi(CH₃)₃, contains Si-H and Si-CH=CH₂ as latent functionality, and its pyrolysis under argon to 1200°C

gave a 57% ceramic yield of SiC and an excess of free carbon. The pyrolysis chemistry of this polysilane is interesting. The Si-H functionality, as observed by infrared spectroscopy, disappears below 300°C, very likely due to thermally-induced Si-H addition to the vinyl groups, to give a cross-linked structure. The Si-H function is observed to reappear around 400°C. This most probably is due to a thermal rearrangement of the type that occurs with $[(CH_3)_2Si]_x$ in the Yajima process. This would represent a second stage of cross-linking.

A different approach was taken by workers at Dow Corning Corporation who prepared their polysilane by the quaternary phosphonium salt-catalyzed redistribution of the methylchlorodisilanes produced as by-products in the synthesis of methylchlorosilanes by the reaction of methyl chloride with silicon-copper alloy.²⁶ Such catalyzed redistribution of the $(CH_3)_nCl_{6-n}Si_2$ ($n = 2,3$) compounds gives volatile methylchlorosilanes, $(CH_3)_nCl_{4-n}Si$, and a polysilane that contains methyl and chlorine substituents on silicon. At the reaction temperatures (up to 250°C) used, the chemistry is complex, and, instead of linear polysilanes, polycyclic products are obtained. One possible structure suggested by Baney, Gaul and Hilty is shown in Figure 4. Alkylation of these polysilanes with alkyl- or aryl-Grignard reagents or reduction with lithium aluminum hydride gave polysilanes in which the chlorine substituents had been replaced by an organic group or hydrogen. These polysilanes could be melt-spun, cured in the solid state and pyrolyzed to produce ceramic fibers. The ceramic product can range from SiC plus excess free carbon to SiC plus excess free silicon; the composition is determined by the substituent introduced in place of the chlorine atoms on silicon in the initially prepared polysilane.

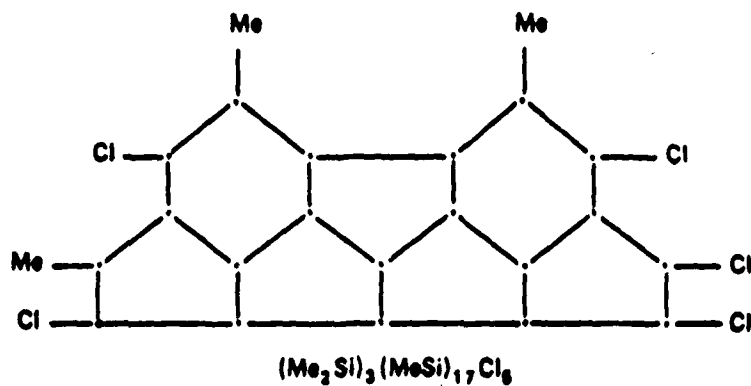


Figure 4. Possible structure for seven-ring polysilane $(\text{Me}_2\text{Si})_3(\text{MeSi})_{17}\text{Cl}_8$; ●, MeSi.

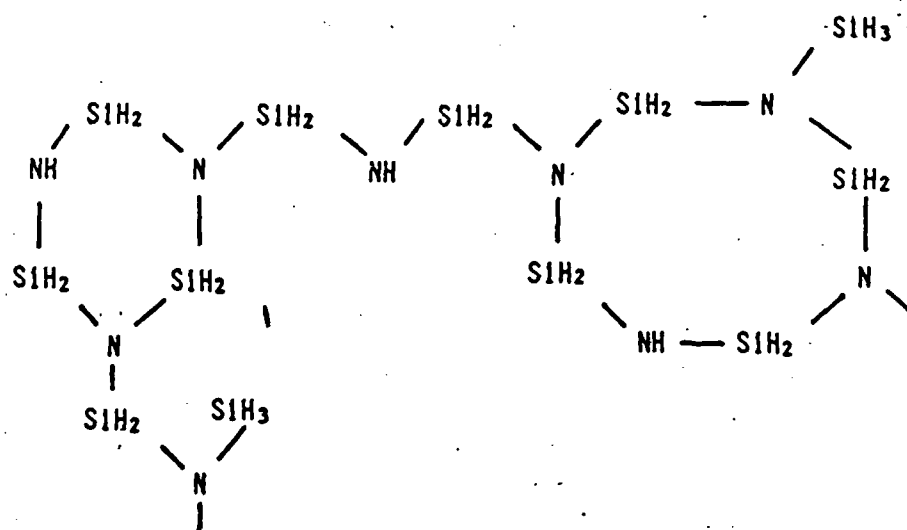


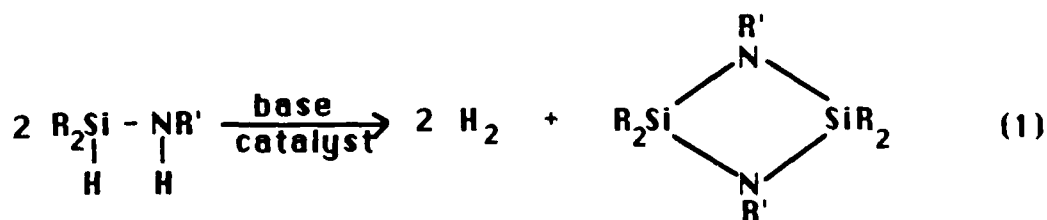
Fig. 5. Suggested structure of the perhydropolysilazane.

A polymeric precursor for silicon nitride also was developed in the Dow Corning Laboratories. Its preparation uses the reaction of trichlorosilane, HSiCl_3 , with hexamethyldisilazane, $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$.²⁷ Trimethylchlorosilane is eliminated in this reaction and is distilled off, leaving a three-dimensional polymer of composition $[(\text{HSi})_{39.7}(\text{Me}_3\text{Si})_{24.2}(\text{NH})_{37.3}(\text{N})_{2.26}]_x$. This polymer could be melt-spun into fibers and a subsequent cure involving treatment with trichlorosilane served to render the polymer infusible and to remove a portion of the Me_3Si groups. Pyrolysis to 1200°C under nitrogen gave ceramic fibers in 65-70% ceramic yield. These were amorphous. Their elemental analysis led to a "composition" of $1 \text{ Si}_3\text{N}_4 + 0.33 \text{ SiC} + 0.12 \text{ SiO}_2 + 0.22 \text{ Si}$, but these discrete species were not really present, the silicon atoms being randomly bonded to C, N and O. Some free carbon was present.

Another route to silicon nitride fibers came from research carried out in the laboratories of the Toa Nenryo Kogyo Company in Japan.²⁸ The reaction of dichlorosilane, H_2SiCl_2 with ammonia, a reaction first described by Stock and Somieski in 1921²⁹ and used in our research at M.I.T. in our first efforts in the preceramic polymer area to develop a precursor for silicon nitride,³⁰ was carried out by Arai and Isoda under conditions that served to give a product of higher molecular weight. Rather than dichlorosilane itself, the H_2SiCl_2 -pyridine adduct was used as starting material and the reaction with ammonia was carried out in dilute pyridine solution. The product was a solid perhydropolysilazane, probably cross-linked to some extent, that was soluble in organic solvents. The polymer could be dry-spun with an organic polymer as spinning aid. Subsequent pyrolysis to 1000°C gave silicon nitride fibers in about 80% ceramic yield. Proton NMR studies showed that the

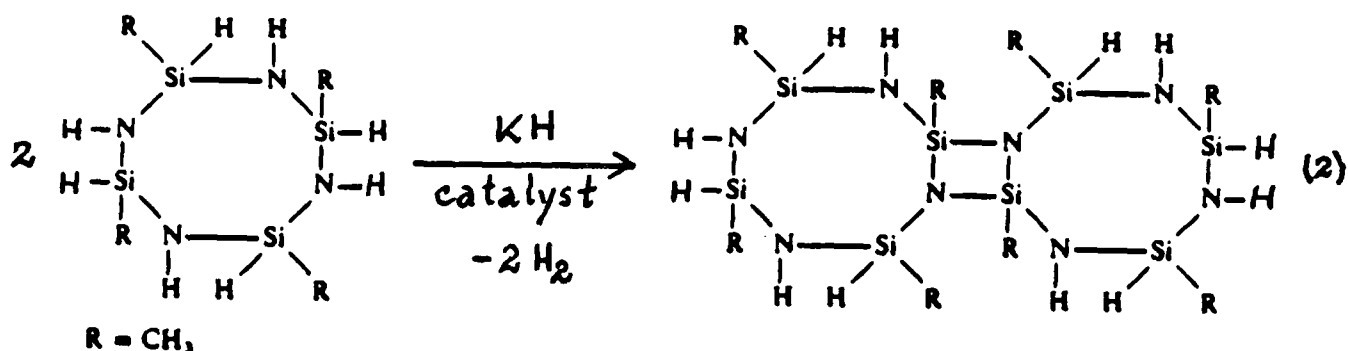
perhydropolysilane was not $[\text{H}_2\text{SiNH}]_x$ as might have been expected, and its composition of $[(\text{H}_2\text{SiNH})_{0.46}(\text{H}_2\text{SiN})_{0.36}(\text{H}_3\text{Si})_{0.18}]_x$ was indicative of more complicated chemistry. This led to the assumed structure shown in Figure 5.

The research that my graduate student and postdoctoral coworkers at M.I.T. have carried out in the preceramic polymer area during the past eight years has been largely focused on the development of precursors for silicon-containing ceramics, principally silicon nitride and silicon carbide. Noteworthy in terms of potentially useful applications are the polysilazanes obtained from methyldichlorosilane, $\text{CH}_3\text{SiHCl}_2$, either alone or in combination with other di- and trichlorosilanes.¹³ Since the ammonolysis of methyldichlorosilane gives low molecular weight, mostly cyclic, oligomers that are not suitable as ceramic precursors, their conversion to material of higher molecular weight was required. Instead of ring-opening polymerization, which is a standard method of converting cyclic compounds to polymers, we applied a process that we call "dehydrocyclodimerization" to the polymerization of these silazane oligomers. This reaction was first applied in small molecule organosilicon chemistry:³¹



Applied to the ammonolysis products of methyldichlorosilane, in which each cyclic silazane contains several sets of adjacent Si-H and N-H bonds, this reaction results in a "ring fusion" polymerization. Using the eight-membered

cyclotetrasilazane as an example, the first step of the process would be that shown in equation 2.



However, it is readily apparent that this chemistry can occur with each Si(H)-N(H) unit in the tricyclic product and that this could result in formation of a sheet network polymer. Using potassium hydride as the basic catalyst, the liquid ammonolysis product of methyldichlorosilane is rapidly and quantitatively polymerized with evolution of dihydrogen. When the reaction is carried out in tetrahydrofuran solution and the reaction mixture is quenched with methyl iodide, a white solid is obtained that is soluble in all common nonprotic organic solvents, including hexane. The addition of methyl iodide is necessary since the dehydrocyclodimerization reaction, under the reaction conditions used, proceeds only to about 60% conversion. At that point, the polymer in solution contains reactive Si(H)-N(K) groups to the extent of the amount of KH catalyst used. Thus it is a "living polymer" and it

must be "killed" by adding methyl iodide or a chlorosilane prior to its isolation. In a typical preparation, proton NMR study of the CH_3I -quenched polymer gave a composition $[(\text{CH}_3\text{SiH}\text{NH})_{0.39}(\text{CH}_3\text{SiN})_{0.57}(\text{CH}_3\text{SiHNK})_{0.04}]_x$, i.e., 57% conversion had been effected. The remaining $\text{Si}(\text{H})\text{-N}(\text{H})$ units undergo thermal H_2 elimination when the polymer is pyrolyzed, and when the pyrolysis to 1000°C is carried out in a stream of argon, a black ceramic residue is obtained in yields of up to 85%. Details of the product of this pyrolysis and of the pyrolysis carried out instead in a stream of ammonia have been mentioned earlier in this review. Preliminary studies at M.I.T. and elsewhere have shown that this polysilazane finds useful application as a binder for ceramic powders, as a precursor for ceramic coatings and for ceramic matrices in composites. Because of the facile further elimination of dihydrogen during even mild heating, it cannot be melt-spun. Dry-spinning is possible but not entirely satisfactory. However, by using the comonomer approach, by cutting back on the reactive $\text{Si}(\text{H})\text{-N}(\text{H})$ functionality by introduction of another chlorosilane of type $(\text{CH}_3)(\text{R})\text{SiCl}_2$, where R is not hydrogen, for instance, $\text{CH}_3(\text{CH}_2=\text{CH})\text{SiCl}_2$, into the original ammonolysis reaction, the subsequent dehydrocyclodimerization reaction will give polysilazanes that can be melt-spun. The "living polymer" intermediate in the dehydrocyclodimerization reaction has an interesting and useful chemistry of its own that has led us to the synthesis of other useful classes of organosilicon preceramic polymers such as precursors for SiC-rich blends of Si_3N_4 and SiC and for silicon oxynitride.^{13c,d} However, a discussion of that chemistry is beyond the scope of the present review.

Preceramic polymer chemistry, especially as applied to the synthesis of precursors for silicon-containing ceramics, has become a very active field of

research, with many groups throughout the world in industrial laboratories, in university laboratories and in government research institutes in vigorous competition. Much of this work is hard to assess because it has been described only in patents or in abstracts of oral or poster presentations at meetings. However, the examples of preceramic polymers that are further along in terms of the development of useful applications that are given above will serve to show the reader how the field has progressed. What is noteworthy in every case is our lack of knowledge of the detailed structure of the preceramic polymers that are discussed. This is in marked contrast to organic polymer chemistry in which our knowledge of the structures of addition and condensation polymers is well developed. This is, perhaps, not surprising. The "good" preceramic polymer is one that already is somewhat cross-linked, thus somewhat complex in structure and hence difficult to study. An example is our polysilazane derived by the dehydrocyclodimerization reaction. The intermediate in this chemistry, the ammonolysis product of methylchlorosilane, is already rather complex: it contains a mixture of $(\text{CH}_3\text{SiH}_2\text{NH})_n$ cyclics ($n = 3,4,5,6\dots$); since the silicon atoms have two different substituents, CH_3 and H , there will be cis and trans isomers of the cyclic compounds; there may also be some linear material and possibly even some cross-linked species if solvent removal has not been carried out carefully. This melange then is treated with KH catalyst to effect polymerization. It is not surprising that the NMR spectra tell us what is present in terms of component groups ($\text{CH}_3\text{SiH}_2\text{NH}$, CH_3SiH and $\text{CH}_3\text{SiH}_2\text{NCH}_3$ from the CH_3I quench) but do not provide a detailed structure of the polymer.

The structure of linear polymers generally is easily elucidated, but these, as noted already, usually are not of interest as ceramic precursors. In view of

the great interest in ceramic fibers, it is ironic that this is so. It is the high molecular weight, linear organic polymers that are the best fiber formers. But it is the substantially cross-linked (nonlinear), generally relatively low molecular weight polymers that are the best ceramic precursors. Thus the polymer properties that satisfy the requirements for good spinnability on the one hand and for high ceramic yield on pyrolysis on the other are mutually exclusive. It is not surprising that the development of satisfactory procedures for the spinning of preceramic polymers is a difficult task and that the properties of the resulting green fibers generally leave something to be desired. Also a source of concern to those who work in the preceramic polymer field is our lack of knowledge about our ceramic products. In many cases, when pyrolysis is carried out to temperatures of 1000°C to 1300°C, the ceramic product is amorphous and difficult to study. However, a detailed understanding of this amorphous, low density and high porosity state of matter is worthwhile and necessary, as noted above.

This discussion has focused on polymeric precursors for silicon-containing ceramics, mainly because most of the activity has been in this area. However, polymeric precursors for other ceramics are of interest and are receiving attention in laboratories throughout the world. Among the nonoxide ceramics of special interest because of their outstanding properties, be these mechanical properties such as hardness, strength or toughness, electrical properties, thermal properties or inertness toward corrosion and high temperature oxidation, are the carbides, nitrides, borides and silicides of many elements. Thus there is active research on polymeric precursors for boron nitride and boron carbide, aluminum nitride, titanium carbide and nitride, as well as the carbides and nitrides of other early transition metals.

Those who work in the organosilicon area have the great advantage of the availability of many organosilicon intermediates on an industrial scale at a relatively low cost. Compare this with research in the organoboron area in which the borazines that often serve as starting materials have to be laboriously prepared in the laboratory of the researcher. On the other hand, in the case of our decaborane(14)-diamine polymers, which are excellent precursors for boron nitride and boron carbonitride and have demonstrated useful applications, decaborane(14) is not readily prepared in the laboratory; its supplies are limited and when purchased, it costs \$2000 a pound for impure material. Nonetheless, we may expect exciting advances in the preceramic chemistry of elements other than silicon in future years.

We have not included oxide ceramics in this discussion. However, the sol-gel route for the preparation of metal oxide powders, coatings and fibers involves polymeric intermediates derived from the hydrolysis, under carefully controlled conditions, of metal alkoxides and other oxy-organic metal derivatives. The metal oxides prepared by such reactions range from pure metal oxides such as SiO_2 and Al_2O_3 to two and multimetal species such as barium titanate. This approach also is being used in the preparation of the new metal oxide superconductors. We do not have the space to cover the sol-gel approach in this article and the reader is referred to introductory reviews of this subject.³²

In conclusion, it should be noted that the area discussed above is one in which chemistry and materials science (more specifically, ceramics) overlap. I have discussed this area in terms of chemistry since I am a chemist. However, a chemist or a ceramist cannot conduct research in this area in isolation. The chemist and ceramist must communicate and collaborate. As the chemistry is

developed, there are important ceramics issues to be addressed. "Good" chemistry does not necessarily guarantee "good" ceramics. However, most likely the chemistry can be modified so that "good" ceramics can be achieved.

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